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Synthesis and structural characterisation of a boralumoxane capable of activating a zirconocene ethene polymerisation catalyst

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Supporting material

to: "Synthesis and structural characterisation of a boralumoxane capable of activating a zirconocene ethene polymerisation catalyst"

by: Richter, Meetsma, Hessen and Teuben

Experimental section

General.

All experiments were performed under inert atmosphere (dinitrogen or vacuum) using standard Schlenk, dry-box and vacuum line techniques. Solvents were purified by passing them under nitrogen atmosphere over columns of Al_2O_3 , molecular sieves (4 Å) and BASF R3-11 oxygen scavenger (pentane, hexane and toluene, Aldrich Anhydrous), or by distillation from Na/K alloy (benzene). Deuterated solvents (benzene- d_6 , toluene- d_8) were dried on Na/K alloy and vacuum transferred before use. ArB(OH)_2 (Ar = 2,6-diisopropylphenyl) was prepared according to the route described in *Org. Synth.* 1959, **39**, 3. Bu^t_3Al (UCFCMO, Germany) was used as purchased. Ethene (AGA polymer grade) was passed over molecular sieves (4 Å) and BASF R3-11 oxygen scavenger before being fed to the reactor. GPC analyses of polyethene were performed on a Polymer Labs PL-GPC210 instrument at 135°C in 1,2,4-trichlorobenzene solvent, using polystyrene and polyethene standards. NMR spectra were recorded on a Varian Unity 500 spectrometer, IR spectra on a Mattson-4020 Galaxy FT-IR spectrometer. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of $[\text{Bu}^t_2\text{Al(O)BAr(OH)}]_2$ (**1**).

A suspension of 0.73 g (3.54 mmol) of ArB(OH)_2 (Ar = 2,6-diisopropylphenyl) in 10 ml of n-pentane was frozen in liquid nitrogen. Bu^t_3Al (0.70 g, 3.54 mmol) was added to the frozen mixture. The suspension was thawed out and stirred for 1 hour at ambient temperature. The precipitate was filtered off and washed with 2 portions of 10 ml n-pentane. Drying the white crystalline solid in vacuum yielded 1.02 g (1.47 mmol, 83%) of analytically pure **1**.

Elemental analysis for $\text{C}_{40}\text{H}_{72}\text{O}_4\text{B}_2\text{Al}_2$ (692.58) found (calcd) %: C, 69.8 (69.4); H, 10.6 (10.5). IR (KBr, cm^{-1}): 3590.8 (w, ν_{OH}), 2959.9 (vs), 2830.4 (vs), 2761.4 (w), 2677.6 (w), 1599.3 (w), 1564.6 (s), 1529.9 (vs), 1464.5 (s), 1384.9 (w), 1199.8 (vs), 959.9 (s), 811.7 (s), 753.6 (s), 661.9 (w), 603.7 (w), 504.2 (w), 411.6 (w). $^1\text{H-NMR}$ (500 MHz, C_6D_6 , 298 K): δ 7.22 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1 H, *p*-H), 7.05 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2 H, *m*-H), 4.73 (s, 1 H, OH), 3.24

(sept, $^3J_{\text{HH}} = 7.0$ Hz, 2 H, CHMe_2), 1.38 (br, 6 H, CHMe_2), 1.28 (br, 6 H, CHMe_2), 1.11 (s, 18 H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6 , 298 K): δ 151.2 (*o*-ArC), 130.6 (*p*-ArCH), 123.3 (*m*-ArCH), 35.8 (CHMe_2), 30.0 (CMe_3), 26.8 (br, CHMe_2) 25.0 (br, CHMe_2), carbons directly attached to B and Al were not observed. ^{11}B -NMR (160 MHz, C_6D_6 , 298 K): δ 21.5 ($W_{1/2} = 1500$ Hz). ^{27}Al -NMR (130 MHz, C_6D_6 , 298 K): δ 128.6 ($W_{1/2} = 18.9$ kHz).

Synthesis of $[\text{Bu}^t\text{Al}(\text{O})\text{BAr}(\text{OLi})]_2 \cdot (\text{C}_6\text{H}_6)_2$ (**2**·(C_6H_6)₂).

To a solution of **1** (0.86 g, 1.24 mmol) in 20 ml of benzene was added 1.0 ml (2.5 mmol) of 2.5 M Bu^nLi in hexane at ambient temperature. The resulting suspension was stirred overnight. The supernatant was decanted and the crystalline solid was dried in vacuum to afford 0.76 g (0.88 mmol, 71 %) of **2**·(C_6H_6)₂.

Elemental analysis for $\text{C}_{52}\text{H}_{82}\text{O}_4\text{B}_2\text{Al}_2\text{Li}_2$ (860.64) found (calcd): %C = 71.9 (72.6), %H 9.7 (9.6). ^1H -NMR (500 MHz, Toluene- D_8 , 298 K): δ 7.18 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2 H, *p*-H), 7.14 (s, 12H, C_6H_6), 7.07 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4 H, *m*-H), 3.52 (sept, $^3J_{\text{HH}} = 7.0$ Hz, 4 H, CHMe_2), 1.44 (br, 12 H, CHMe_2), 1.28 (br, 12 H, CHMe_2), 1.02 (s, 36 H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, Toluene- D_8 , 298 K): δ 151.8 (*o*-ArC), 137.7 (*p*-ArCH), 128.8 (C_6H_6), 124.2 (*m*-ArCH), 34.7 (CHMe_2), 32.1 (CMe_3), 26.9 (br, CHMe_2) 26.3 (br, CHMe_2), carbons directly attached to B and Al were not observed. ^{11}B -NMR (160 MHz, Toluene- D_8 , 298 K): δ 25.6 ($W_{1/2} = 2900$ Hz). ^{27}Al -NMR (130 MHz, Toluene- D_8 , 298 K): δ 116.1 ($W_{1/2} = 5600$ Hz).

Synthesis of solvent-free $\text{Al}(\text{Bu}^t\text{Al})(\text{Bu}^t\text{Al})_2(\text{O}_2\text{BAr})_4$ (**3**).

A suspension of 0.50 g (0.72 mmol) of **1** in 10 ml *n*-hexane was refluxed for 2 hours. The warm solution was filtered to remove traces of insoluble material. The solution was allowed to stand overnight at ambient temperature, affording 0.12 g of **3** as colorless crystals. The mother liquor was cooled to -30 °C, yielding another 0.08g of **3**. Overall yield: 0.20 g (0.17 mmol, 48%) of solvent-free $\text{Al}(\text{Bu}^t\text{Al})(\text{Bu}^t\text{Al})_2(\text{O}_2\text{BAr})_4$ (**3**).

Elemental analysis for $\text{C}_{64}\text{H}_{104}\text{O}_8\text{B}_4\text{Al}_4$ (1152.7) found (calcd): %C = 66.9 (66.7), %H 9.3 (9.1). IR (KBr, cm^{-1}): 3504.9 (w), 2962.9 (vs), 2930.3 (s), 2872.2 (s), 2837.4 (s), 1593.9 (w), 1462.9 (vs), 1385.3 (vs), 1297.0 (s), 1177.1 (s), 989.4 (s), 809.1 (w), 760.3 (w), 688.2 (w), 646.6 (w), 596.4 (w), 452.2 (w). ^1H -NMR (500 MHz, Toluene- D_8 , 298 K): δ 7.26 (t, $^3J_{\text{HH}} = 8.0$ Hz, 2 H, *p*-H), 7.13 (m, 6 H, *p*-H and *m*-H), 7.02 (d, $^3J_{\text{HH}} = 8.0$ Hz, 4 H, *m*-H), 3.31 (sept, $^3J_{\text{HH}} = 6.5$ Hz, 2 H, CHMe_2), 3.27 (sept, $^3J_{\text{HH}} = 6.5$ Hz, 2 H, CHMe_2), 3.23 (br, 4 H, CHMe_2), 1.49 (br, 12 H, CHMe_2), 1.40 (br, 24 H, CHMe_2), 1.33 (br, 12 H, CHMe_2), 1.16 (s, 18 H, CMe_3), 0.56 (s, 18 H, CMe_3). ^{13}C -NMR (75 MHz, Toluene- D_8 , 298 K) δ 153.4 (*o*-ArC), 153.0 (*o*-ArC), 131.4 (*p*-ArCH), 130.9 (*p*-ArCH), 123.1 (*m*-ArCH), 123.0 (*m*-ArCH), 36.2 (br, CHMe_2), 35.9 (CHMe_2), 35.8 (CHMe_2), 30.5 (CMe_3), 29.3 (CMe_3), 26.4 (br,

CHMe_2), 25.7 (CHMe_2), carbons directly attached to B and Al were not observed. ^{11}B -NMR (160 MHz, Toluene- D_8 , 298 K) δ 31.9 ($W_{1/2} = 2960$ Hz). ^{27}Al -NMR (130 MHz, Toluene- D_8 , 298 K): δ 49.8 ($W_{1/2} = 7650$ Hz). ^{27}Al -NMR (130 MHz, Toluene- D_8 , 353 K): δ 123.3 ($W_{1/2} = 34.5$ kHz), 50.3 ($W_{1/2} = 3550$ Hz).

Synthesis of $\text{Al}(\text{Bu}^t\text{Al})(\text{Bu}^t\text{Al})_2(\text{O}_2\text{BAr})_4(\text{C}_6\text{H}_6)_{2.5}$ (3**·(C_6H_6) $_{2.5}$).**

On a vacuum line, a suspension of $\text{ArB}(\text{OH})_2$ (Ar = 2,6-diisopropylphenyl, 0.58 g, 2.83 mmol) in 10 ml of toluene was degassed and then frozen with liquid N_2 . Subsequently, Bu^t_3Al (0.56 g, 2.83 mmol) was condensed into the reaction mixture, after which the mixture was thawed out and stirred at ambient temperature for 1 h. Then the temperature was raised to 50 °C and the solution was stirred for 2 more hours. After stirring at ambient temperature overnight, all volatiles were removed in vacuum. The remaining white solid was suspended in 20 ml of benzene and stirred at ambient temperature for 5 days. The suspension was then briefly warmed to 40 °C to give a clear solution, which was filtered and concentrated, resulting in the separation of colourless needles. Crystals suitable for X-ray analysis were obtained. The crystalline solid was filtered off and dried in vacuum to afford of **3** as its benzene solvate. Yield: 0.75 g (1.12 mmol, 79%) of $\text{Al}(\text{Bu}^t_2\text{Al})(\text{Bu}^t\text{Al})_2(\text{O}_2\text{BAr})_4(\text{C}_6\text{H}_6)_{2.5}$ (**3**·(C_6H_6) $_{2.5}$). The NMR spectra of this material are identical to that of solvent-free **3** (apart from the presence of C_6H_6).

Ethene Polymerisation (general procedure).

In a dry-box, equimolar amounts of solid Cp_2ZrMe_2 and the appropriate boralumoxane were weighed out and subsequently dissolved in toluene. The toluene solutions (with a combined volume of 20 ml) were mixed in a glass 50 ml Büchi 'Tiny Clave' reactor equipped with a magnetic stirring bar. The reactor was connected to an ethene supply line and charged with 5 bar ethene. The reaction mixture was stirred at 900 rpm for 30 minutes at ambient temperature, during which ethene was continuously supplied to the reactor. The reaction was stopped by venting the reactor and quenching the reaction mixture with ethanol. The polymer was filtered off on a glass frit, washed with ethanol and dried overnight at 80 °C in a vacuum oven. Results of the runs performed are listed in the table below.

Run no. ^{a)}	Cocatalyst (μmol)	Cp_2ZrMe_2 (μmol)	PE (g)	Productivity (kg/mol.h.bar)	M_w	M_w/M_n
1	1 (91.5)	91.0	0.0	0		
2	1 (91.4)	88.6	0.0	0		
3	3 (50.1)	50.1	0.32	2.6	16600	1.85
4 ^{b)}	3 (32.9) ^a	32.9	0.20	2.4	15300	1.87

^{a)} Conditions: 20 ml toluene, 5 bar ethene, ambient temperature, 30 min. run time.

^{b)} Performed in 13 ml of toluene (concentrations of Zr and Al identical to those in run no.3)